

PERSISTENT ORGANIC POLLUTANTS IN THE ATMOSPHERE OF TWO ANTARCTIC ZONES (ANTARCTIC PENINSULA AND ROSS SEA) USING PASSIVE AIR SAMPLERS (PUF DISKS)

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Introduction

Persistent organic pollutants (POPs) are a global environmental concern. The Stockholm Convention (SC) on POPs aims to reduce or eliminate the use, discharge and emission of these compounds to the benefit of the environment, reducing risks to humans and wildlife¹. Currently, 23 chemicals are listed under the SC, including the original 12 “legacy POPs” (e.g. organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-dioxins/dibenzofurans (PCDD/Fs)) and several newly listed POPs.

The transport of POPs to polar regions is complex and occurs through meteorological transport events and through a more gradual cycling process involving successive volatilization and deposition steps from warmer areas towards cooler regions. Because of the low temperatures and limited solar radiation, the environmental residence time of organic contaminants is generally longer in polar regions than at lower (warmer) latitudes². The Antarctic region covers about 20% of the southern hemisphere. The primary input of POPs to Antarctica is through long-range atmospheric transport (LRAT). Nevertheless, literature data on POPs in the atmosphere of Antarctica is relatively scarce compared to other parts of the world. This is due largely to high costs and logistical challenges (e.g. source of electricity) associated with conventional air sampling methods³. During the last decade passive air samplers (PAS) have become widely used to address these challenges and to generate better spatially resolved data for studying the occurrence and transport of POPs at local, regional and global scales³⁻⁴. In 2010-2011, as part of an international collaboration project between several research groups operated under the Chilean Antarctic institute (INACH) and the Italian Antarctic Research Programme PAS consisting of polyurethane foam (PUF) disks were deployed at two Antarctic stations - the Chilean station near the Antarctic Peninsula (northern) and the Italian station on Ross sea coast (east side of Antarctica). The purpose of the study was to assess long range transport of POPs and their concentration and spatial patterns in air.

Material and methods

Study area

The Antarctic Peninsula stations (northern stations) included: Professor Julio Escudero Base (ESC) close to King George Island, the Captain Arturo Prat Base (AP) located on Greenwich Island, and the O'Higgins Station (OS), which is the only permanent Chilean station on the Antarctic mainland (Figure 1a). The Mario Zucchelli Station (74°42' S, 164°07' E) is the Italian coastal research station located in east Antarctica, at Terra Nova Bay. The scientific activities have been ongoing at the base since 1986, mainly during the spring and summer seasons (October -February). Six stations are currently established at the Italian base including: Lucia-Larsen glacier (LU), Eneide-Terra Nova Bay (EN), Alessandra-Cape King (AL), Penguin-Edmonson Point (PE), Sofia B-David Glacier (SO), and Modesta-Alto Priestley (MO) (Figure 1b).

Sampling

Sampling was conducted using PUF disks or sorbent impregnated polyurethane foam (PUF) disk (i.e. SIP disk) which in previous studies have been shown to produce comparable results⁴. Duplicate samplers were deployed at 3 sampling sites on the northern peninsula (January-June 2010) and at 6 sites near the Ross Sea coast

(December 2010-January 2011). Details regarding the preparation and deployment of PUF disk type samplers is provided elsewhere^{3,4}.

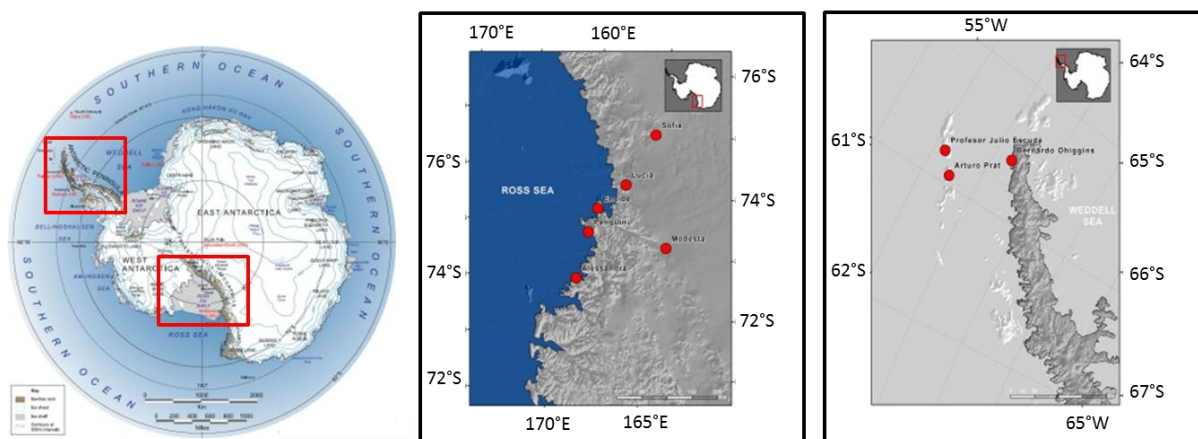


Figure 1. Map showing sampling at sites operated by a) Chile (northern Antarctic Peninsula) (ESC=62° 12' 4" S, 58° 57' 45" W; OS=63° 19' 18" S, 57° 53' 57" W; AP= 62° 28' 44.45" S, 59° 39' 54.28" O) and b) Italy (Ross Sea coast, East Antarctica) (LU=74° 57' 01.7" S, 161° 46' 14.5" E; EN=74° 41' 45.33" S; 164° 05' 31.83"E; AL=73° 35' 09.93" S, 166° 37' 15.75" E; PE=74° 20' S, 165° 08' E; SO=75° 36' 41.91" S, 158° 35' 25.64" E; MO= 73° 38' 21.19" S, 160° 38' 44.36" E).

Extraction and clean-up of samples

Samples were extracted as reported previously³⁻⁴ using Soxhlet extraction system. The extract was reduced under a stream of nitrogen to about 10 mL and split into 2 aliquots. The aliquot for POPs determination was cleaned-up on a glass column filled with 1g AgNO₃ and 5 g 44% H₂SO₄ silica. The extract was loaded and eluted with 40 mL DCM:*n*-hexane mixture. The solvent was reduced in TurboVap II and transferred into a GC conical vial and internal standards (ISTD) were added.

Chemical analysis

Samples were analyzed for a suite of target compounds that included 7 indicator PCBs congeners (PCB-28, -52, -101, -118, -153, -138, -180), 10 pesticides including: *p,p'*-DDT, *p,p'*-DDD, and *p,p'*-DDE, α -, β -, γ -, δ -, ϵ -hexachlorocyclohexane (HCH), hexachlorobenzene (HCB) and pentachlorobenzene (PeCB). GC-MS/MS was used for indicator PCBs and OCPs analysis. 7890A GC (Agilent, USA) equipped with a 60m x 0.25mm x 0.25um HT8 column (SGE, USA) coupled to 7000B MS (Agilent, USA) operated in EI+ MRM was used. Injection was splitless 3 μ L at 280°C, He as carrier gas at 1.5 mL min⁻¹. The GC temperature programme was 80°C (1 min hold), then 40°C min⁻¹ to 200°C, and finally 5°C min⁻¹ to 305°C. Chemical analyses were conducted at Masaryk University, Research Centre for Toxic Compounds in the Environment (RECETOX), Brno, Czech Republic. Method detection limits (MDL) in air samples were defined as the average blank (n=9) plus three standard deviations (SD). When target compounds were not detected in blanks, 1/2 the instrumental detection limits (IDL) value was substituted for the MDL. All qualified data (i.e., exceeding the MDL) have been blank corrected. Levels in blanks were generally less than 20% of the amounts in samples.

Results and discussion

Figure 2 summarizes concentrations in air for PCBs and OCPs at the two Antarctic stations. Concentrations were derived by dividing the amount of chemical collected on the PUF disks by the product of the deployment period and using a sampling rate of 4 m³d⁻¹ previously derived by Pozo et al.³. Results Σ PCBs_(7 PCB indicators) (pg m⁻³) ranged from ~1 to 4 at sites on the northern peninsula and about 20 times lower (less than 1 pg m⁻³) at sites near the Ross Sea coast. The PCB congener pattern was different at the two Antarctic stations, showing a prevalence of low to middle chlorinated PCBs (PCB-28,-52 and -101) in the northern station while at the Ross Sea sites, higher molecular weight PCBs (PCB-118, -153, -138, -180) were preferentially detected.

The concentrations of PCBs in air are in the same range than those recently reported at the Norwegian Troll station² (~0.5 pg m⁻³) during 2007-2010 (sum of 10 congeners), and in King George Island (KGI) (2-8 pg m⁻³)⁵

during 2004-2005 (sum of 31 congeners). Much higher levels of PCBs were reported during the early 1990s at Admirantly Bay (in KGI) by Montone et al.,⁶ with concentrations in the range of ~10-90 pg m⁻³. The apparent reduction in PCB concentration in air may be attributed to PCB restrictions in major PCB source areas prior to and under the SC. We note that neighbouring countries such as Chile and Argentina account for only 0.1% and 0.5%, respectively, of the global historical PCB production². Although LRAT to Antarctica from other continents has been suggested as the main source of POPs, some studies indicate that this transport pathway is not efficient due to strong westerlies in the mid latitudes, 40–60° S, which isolate the continent during the winter⁷. This has also been observed in this study by conducting trajectory simulation, using the HYSPLIT model⁸ (2 trajectories per day, followed 20 days back in time): The majority of air masses arriving on the Antarctic peninsula were advected from south-west (following the westerlies). Few travelled from the southwest, curving over south Chile and over the Antarctic continent. Concerning the Ross Sea sites, the majority of the air masses arrived from the polar low via crossing Central and (less) West Antarctica. No trajectories passed over any other continent. This analysis suggest that regional sources dominated pollution on the Antarctic Peninsula. Potential sources include activities associated with military stations, tourism and research stations (including ship-based and air-based transport). A similar finding was concluded for contamination of a coastal site in East Antarctica during 2002-2005⁹.

Among the targeted OCPs, HCB showed the highest concentrations in air confirming its long lifetime and ubiquitous distribution in the atmospheric environment. In particular, lower HCB concentrations (pg m⁻³), were detected at the Peninsula, northern stations (~1-15) and higher values at Ross Sea sites (1-50). These results agree with reported values by Kallenborn et al.,² at Troll station during 2007-2010 sampling campaign (~23 pg m⁻³) and are also similar to the levels reported by Dickhut et al.,¹⁰ during 2001 air sampling (5 to 30 pg m⁻³) on the Ross Sea region and with those reported by Montone et al.,¹¹ in a 1995 sampling campaign (~25 pg m⁻³) in the marine Antarctic atmosphere.

Resulting concentrations in air (pg m⁻³) for other targeted compounds included PeCB (0.01-6) and HCHs and DDTs (0.01-0.08). For the HCHs, α -HCH was detected in both Antarctic zones while γ -HCH was only detected at northern stations (0.01-1). These findings are in agreement with results recently reported by Kallenborn et al.,² at Troll station showing a prevalence of α -HCH, with a factor of 3-4 times higher concentration than for γ -HCH. In the case of DDTs isomers, *p,p'*-DDT was higher at the northern stations (~0.4 pg m⁻³) (only detected at ESC and OS) than the levels at Ross Sea sites (~0.04 pg m⁻³) (only detected at EN, AL, LU). The *p,p'*-DDE ranged from 0.01-0.3 pg m⁻³ in the sites from Antarctic Peninsula (ESC and OS), and was only detected at one site (AL=0.08 pg m⁻³) in the west of Antarctica. When comparing these results with the values reported 20 years ago by Larsson et al.,¹² in Ross Island, it is found that concentrations in air of DDTs are similar (with *p,p'*-DDE= 1 pg m⁻³ and *p,p'*-DDT=2 pg m⁻³).

Although, levels of DDTs are very low. *p,p'*-DDE/*p,p'*-DDT = 1-1.5, however, indicates fresh input of DDT. Possible sources of DDT could be direct intercontinental LRAT from tropical areas where DDT is applied for malaria prevention, such as South Africa. Both DDT and HCH are undergoing LRAT due to long atmospheric lifetimes, even under low temperatures characteristic for polar regions, which favors association to the particulate phase of the atmospheric aerosol, which, in turn limits atmospheric lifetime (particle deposition)². Difference in levels observed between the peninsula and the Ross Sea can be explained by the respective source regions (indicated by the air sheds, see above) i.e., regional transports, with occasional intercontinental transports (south Chile) only in the case of the peninsula sites. Import, manufacture, sale, distribution and use of DDT has been forbidden in Chile since 1984. This suggests that eventually old stock of DDT in the region (Argentina, Brazil and Chile) might have contributed to DDT contamination of the Antarctic Peninsula. Furthermore, air-sea exchange might be a contributing factor, although modelling suggests reversal (to net volatilization) to happen very late if at all in the Southern Ocean¹³.

These results represent one of the very few data sets on the spatial distribution of POPs in Antarctica. The study highlights the feasibility of using passive air samplers for trace analysis of POPs in air while overcoming some of the logistic challenges associated with air sampling in remote polar environments. Passive sampling has the advantage of not requiring electricity which allows samplers to be deployed far away from research stations and other human activities in order to minimize the impact from potential local anthropogenic sources.

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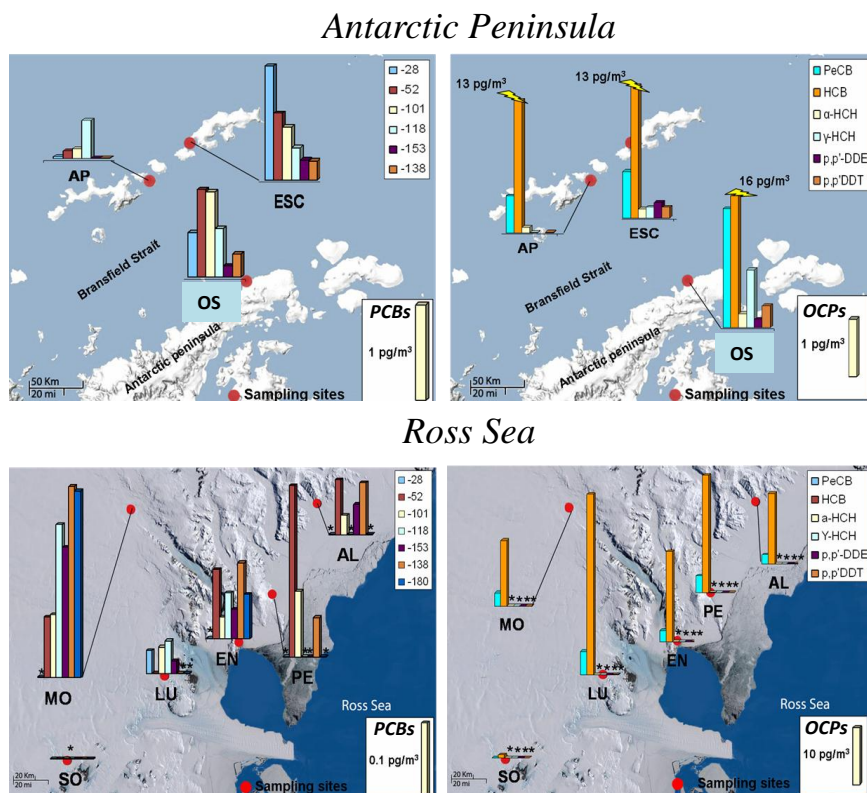


Figure 2. Concentrations in air of individual PCBs and OCPs at Antarctic sampling sites near the Ross Sea (near Italian base) and the Antarctic Peninsula (near Chilean base) during 2010 and 2011.

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